

## Determination of the Distribution of Ash, Pyrite and Basic Constituents in Coal Particles

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### INTRODUCTION

In fluidized-bed gasification of high-sulfur coals, such as the KRW and U-GAS processes, relatively low melting ash is produced by reaction of iron from pyrite with the siliceous components produced from clays and quartz.(1,2) To prevent catastrophic growth of ash clinkers and defluidization of the bed, ash in the bed must be limited to 40 to 50 weight percent. As a result of this low ash content of the bed, the ash must be agglomerated to facilitate its removal from the bed without unacceptable loss of char carbon and decrease of gasification efficiency. To obtain a detailed understanding of the behavior of mineral matter and ash in fluidized-bed gasification, a fundamental research investigation is in progress at IGT under a program supported by the U.S. Department of Energy.(2,3)

In our approach to the problem, we note that pyrite quickly decomposes to ferrous sulfide when the coal is introduced into the hot fluidized bed of a gasifier; also that sufficient hydrogen sulfide is produced from high sulfur coal to stabilize the ferrous sulfide in the back-mixed fluidized bed away from the oxygen inlet region; also that in the back-mixed bed the gasification reactions with steam and carbon dioxide occur relatively slowly and thus tend to occur throughout char particles. Complete removal of the carbon in char particles must occur before the oxidized iron can contact the siliceous components in the ash. Both this carbon removal and the oxidation of the ferrous sulfide occur only in the oxygen inlet region. Elevated temperatures in this region also facilitates the reaction of oxidized iron with the siliceous components to form relatively low-melting iron aluminosilicates. In both the KRW and U-GAS processes, oxygen is introduced through a central jet, forming an oxygen reaction region resembling a burner flame. Thickness, shape, and temperature of this reaction region is known only within wide limits.

We envision that the initial formation of ash reaction products occurs by reaction of the minerals present in single particles of char formed from single particles of coal. The oxide composition of the ash of single particles determines their melting point, viscosity and potential for agglomeration. In this paper we report the results of the application of some methods of investigation of ash composition in single particles of coal.

### Selection of Coals

As part of the research on the behavior of ash in fluidized-bed gasification, several coals were selected for test in a 2-inch reactor. These were five eastern U.S., one western (New Mexico) bituminous, and one subbituminous coal. All had been washed except the subbituminous coal. Four of the eastern U.S. coals were selected to cover a range of iron oxide content of the ash from about 10 to 30 weight percent  $\text{Fe}_2\text{O}_3$  along with a calcium oxide content of 2.5 weight percent or less; the other, an Illinois No. 6 seam coal, was selected to show the effect of high calcium oxide content with low iron oxide. Analytical data pertaining to minerals and ash of the coals, including iron distribution by Mossbauer spectroscopy and mineralogy by computer-assisted scanning electron microscopy (SEM), are presented in Table 1.

Table 1. ANALYSES OF MINERALS AND ASH OF COALS USED IN GASIFICATION TESTS

Seam Mine	KY No. 9 Providence	OH Pitt No. 8 Franklin 125	KY No. 13 Ken No. 13	IL No. 6 Burn. Star 4	IN VI Universal	York York Canyon	Rosebud Rosebud
Ash Composition, wt %							
SiO <sub>2</sub>	54.5	41.6	58.5	54.1	51.1	44.4	48.8
Al <sub>2</sub> O <sub>3</sub>	17.8	20.9	26.9	16.9	21.9	24.3	23.5
Fe <sub>2</sub> O <sub>3</sub>	19.9	31.7	8.1	10.7	15.7	9.0	7.02
TiO <sub>2</sub>	0.80	1.02	0.87	0.70	0.85	1.02	0.12
P <sub>2</sub> O <sub>5</sub>	0.07	0.07	0.16	0.13	0.12	2.11	0.25
CaO	2.29	1.14	0.90	8.34	2.48	8.15	7.16
MgO	0.67	0.36	1.21	0.95	1.18	2.15	2.57
Na <sub>2</sub> O	0.54	0.35	0.24	0.75	0.65	0.90	0.09
K <sub>2</sub> O	2.20	0.98	2.94	1.96	2.85	0.44	0.36
SO <sub>3</sub>	2.10	1.00	0.80	7.00	1.30	5.50	9.91
Total	100.9	99.2	100.6	101.5	98.1	98.0	99.78
Ash Content (as ashed for analysis of ash, dry basis)	7.9	7.7	8.2	13.4	13.5	8.0	
Iron Distribution (by Mossbauer Spectroscopy)*							
Pyrite	92.1	95.8	71.4	91.6	80.5	9.7	--
Clay	--	--	11.2	--	6.9	70.6	--
Siderite	--	--	--	--	--	15.5	--
Ferrous Sulfate <sup>b</sup>	7.9	4.2	--	4.6	tr?	--	--
Ferric Sulfate <sup>b</sup>	--	--	17.4	3.8	12.7	4.2	--
Mineral Distribution (by SEM)*							
	wt % of total minerals						
Quartz	20	11	17	20	23	6	--
Kaolinite	5	10	7	3	3	14	--
Illite	7	11	20	7	18	2	--
Chamosite <sup>c</sup>	--	--	1	<1	<1	8	--
Montmorillonite	<1	1	1	2	1	5	--
Mixed Silicates <sup>d</sup>	22	20	28	23	25	31	--
Pyrite	33	36	17	23	18	1	--
Iron Sulfates	3	2	2	<1	1	--	--
Siderite	<1	<1	<1	--	<1	2	--
Calcite	5	--	<1	16	4	10	--
Ankerite	--	--	--	--	--	1	--
Rutile	<1	1	<1	<1	<1	--	--
Apatite	--	--	--	--	--	2	--
Misc. Mixed	>4	>8	>6	>5	>5	18 <sup>e</sup>	--

\*By G. F. Hoffman and Associates at Macro-Arom, Inc.

<sup>a</sup>FeSO<sub>4</sub>/H<sub>2</sub>O and FeSO<sub>4</sub>/7H<sub>2</sub>O.<sup>b</sup>KFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>.<sup>c</sup>Hydrated magnesium-iron aluminosilicate.<sup>d</sup>Mostly mixed layer clays.<sup>e</sup>Includes many Ca(Sr)-Al(Si)-P particles, possibly crandallite.

### Distribution of Ash Composition Among Particles

Moza and Austin have described the analysis of individual pulverized coal particles by computer-assisted SEM.(4) The objective of this work was the evaluation of coals for slag deposition in electric utility boilers fired with pulverized coal. Sieve fractions of particles from 10 to 106  $\mu$ m in diameter were mounted separately, sectioned and polished; those particle cross-sections falling within the size range of the sieve fraction were selected for x-ray emission analysis; about 280 particles of the coarsest fraction and 800 to 900 of the finest were analyzed.

Moza and Austin's method seems admirable for pulverized fuel, but of doubtful applicability to the 1/4-inch top size feed to fluidized-bed gasifiers. One difficulty is that sections oriented parallel to the coal bedding are not representative of the minerals of the whole particle.

For this investigation, we adopted a chemical method in which the ash compositions of 32 single particles were determined. Particles from the -10+12 mesh fraction of the 1/4 inch top size coal were taken for analysis; this size furnishes enough ash for the chemical analysis and is about the average size, by weight, of the coal feed to a pilot plant or commercial fluidized-bed gasifier. Particle weight, ash content, and iron oxide and calcium oxide in the ash were determined. In addition to determined contents of iron and calcium oxide in the ash, the content of basic constituents was estimated by adding the average amount of other basic oxides ( $MgO$ ,  $K_2O$  and  $Na_2O$ ), as determined by a conventional major and minor oxides analysis, to the determined iron and calcium oxides. A correction for sulfur trioxide in the particle ash was made, based on the average ratio of  $SO_3$  to  $CaO$  in the conventional analysis of the ash of the eastern U.S. coals that we investigated. This method of correction was not satisfactory when the content of calcium oxide in the single particle ash was higher than about 20%.

Analysis of the single particles are reported in detail elsewhere.(3) Averages for the first 16, the second 16, the odd-numbered particles, the even-numbered particles, and for all particles are also listed; the subsets were calculated to obtain a measure of the effect of number of analyzed particles. For eastern bituminous coals, the most important distribution is that of the iron oxide content of the ash. For the Kentucky No. 9 coal, the average iron oxide contents of the four groups of 16 particles ranges from 21.72 to 26.35 weight percent, and the average for all particles is 22.27 weight percent compared to 19.9 weight percent obtained by the conventional analysis for major and minor oxides. We conclude from this and similar data on the other coals that analysis of 32 particles is necessary and may be sufficient for characterizing the distribution.

A comparison of the averages of the particles with the values of the conventional major and minor oxides is presented in Table 2. While the average iron oxide in the ash of the 32 particles of Kentucky No. 9 coal agrees well with the conventional analysis, less than half as much calcium oxide was present in the -10+12 mesh particles as in the conventional analysis. We think that the missing calcium oxide occurs as calcite in the cleat of the coal, along which fracture occurs in crushing and sieving, resulting in its concentration in the finer sieve fractions. Presence of plates of calcite, about 10  $\mu$ m thick, in the cleat fractures of the Kentucky No. 9 coal is shown in a photomicrograph (Figure 1) of a polished section of coal etched by low temperature oxidation to expose the minerals. In the photomicrograph, only the crack normal to the bedding is a cleat fracture; the curved cracks are artifacts produced in the preparation and etching.

Similar loss of calcium oxide from the -10+12 mesh particles is also evident with the Indiana VI coal (Table 2), while 90% of the average 8.34 weight percent of calcium oxide in the ash of the Illinois No. 6 coal has been lost. No loss, or

Table 2. SUMMARY OF SINGLE PARTICLE ANALYSES

	Ash Content (moist basis)		Fe <sub>2</sub> O <sub>3</sub> in Ash		CaO in Ash	
	Avg. of Particles	Conventional	Avg. of Particles	Conventional	Avg. of Particles	Conventional
	wt %					
KY No. 9	6.3	7.6	22.3	19.9	1.10	2.29
Pittsburgh	10.9	7.5	34.2	31.7	1.14	0.90
KY No. 13	8.2	7.3	8.6	8.1	0.69	0.90
IL No. 6	10.3	11.9	12.1	10.7	0.83	8.34
IN VI	16.4	13.4	6.9	15.7	0.36	2.48
Rosebud	10.3	11.3	0.55	7.0	9.4	7.2

only a marginal one, is evident from the Pittsburgh No. 8 or Kentucky No. 13 coals. Neither did it occur with the subbituminous B Rosebud coal in which the calcium occurs dispersed in the organic matter, partly as carboxylate and (probably) partly as calcite from decomposition of calcium carboxylates. However, about 90% of the average amount of iron oxide is absent from the -10+12 mesh particles of this coal. This is in accord with observations on coal from this seam by other investigators; Kuhn *et al.* examined pyrite grains in coal ground to pass a 20-mesh sieve and found that all were unattached to coal.(5) The mean diameter of the pyrite grains was 80  $\mu$ m. Chadwick *et al.* reported that "pyrite in the coal occurs principally as sheets or film on vertical fracture, or cleat, surfaces."(6)

The distributions in the Kentucky No. 9 particles are shown in Figure 2. To prepare a plot, the particle analyses were arranged in the order of increasing amount of the component, such as iron oxide and the cumulative amount of ash for that order was calculated. Note that a different order of the particles is obtained for each component in the ash of a coal. The plots for iron oxide and basic constituents indicate the presence of two different populations, one with iron oxide content up to about 30 weight percent and the other from 20 to 100 weight percent. It appears likely that the first is from attrital coal and mixtures of attrital coal and vitrain, and the second mainly from vitrain only. Vitrain is recognized as shiny black layers or lenses in the coal thicker than 0.5 mm, and is attributed to the coalification of relatively large fragments of wood and bark. Thus it is almost entirely free of particles of minerals except those, such as pyrite, that are deposited from infiltrating solutions or are present in the woody plant. Alternatively, it is possible that the iron-rich particles contain pyrite of a bedding layer adjacent to vitrain; however, this appears unlikely, as the ash in these particles ranges only from 2.3 to 10.0 weight percent.

The distributions in larger and smaller particles than the -10+20 mesh also should be considered. In general, the distribution is expected to become wider (greater deviation from the average) as particle size decreases; and, for example, the number of particles with a single layer, whether attrital coal or vitrain, increases. The opposite may be true of larger particles, but not if the size of particles is less than that of the predominant width of layers. Ashes of individual -4+5 mesh particles of the Kentucky No. 9 coal are shown in the photograph of Figure 3. Large differences in the iron content of the ash is indicated by the white or gray appearance of some, which have little or no iron, in contrast to others that are very dark because of the presence of hematite from pyrite. This suggests that the distribution of iron in -4+5 mesh particles does not differ much from that of the -10+12 mesh particles.

Distributions in the particles of the Pittsburgh No. 8, Kentucky No. 13, and Rosebud coal (except for basic constituents) are shown in Figures 4, 5, and 6. Distributions in the particles of the Illinois No. 6 and Indiana VI coals were similar to those of the Kentucky No. 13.

When a knowledge of jet temperatures and a correlation between composition, temperature, and agglomerating tendency becomes available in the future, the distributions will indicate how much of the ash, after burnoff of the char, is immediately available for agglomeration — that is, without need for combination with the ash of a different particle. At present, it is estimated that, in the absence of more than about 2 weight percent of calcium oxide, ash with iron oxide contents from about 20 to 80 weight percent may fall in this category. This upper limit is expected to decrease with decreasing silica-to-alumina ratio and increasing magnesia content, according to phase diagram considerations.(2)

A summary of the distribution of iron oxide in the ash of the -10+12 mesh particles is presented in Table 3 for the eastern bituminous coals, together with

the average iron oxide content. Ash of Kentucky No. 9 coal, from the same mine as that used here, agglomerated without difficulty in U-GAS pilot plant tests with bed temperatures at about 1870°F. (Temperatures in the jet are substantially higher.) The particle analyses of this coal show 59% of the ash to have 0 to 20 weight percent  $\text{Fe}_2\text{O}_3$  and 38% to have 20 to 80 weight percent  $\text{Fe}_2\text{O}_3$ . Although the ash of the Pittsburgh No. 8 coal has an average  $\text{Fe}_2\text{O}_3$  content of 31.7 weight percent, much higher than that of the ash of the Kentucky No. 9, its fraction of ash in the 20 to 80 weight percent  $\text{Fe}_2\text{O}_3$  range is much lower, only 10%. This suggests that the ash of the Pittsburgh coal should agglomerate more slowly, but its real significance has not been determined as yet. The same is true of the Indiana VI coal, whose total ash has sufficient iron, 15.7 weight percent  $\text{Fe}_2\text{O}_3$ , for agglomeration although very little falls in the 20% to 80% range. The Kentucky No. 13 and Illinois No. 6 coals probably have insufficient iron for agglomeration of their ash, but in this case the ash content of the bed in a gasifier can be allowed to rise to such an extent that very little carbon is ungasified.

Table 3. SUMMARY OF DISTRIBUTION OF  $\text{Fe}_2\text{O}_3$  IN -10+12 MESH PARTICLES OF EASTERN BITUMINOUS COALS

Coal	Avg. $\text{Fe}_2\text{O}_3$ Content, wt %	0-20% $\text{Fe}_2\text{O}_3$ % of ash	20-80% $\text{Fe}_2\text{O}_3$ % of ash	80-100% $\text{Fe}_2\text{O}_3$
Kentucky No. 9	19.9	59	38	3
Pittsburgh No. 8	31.7	61	10	29
Kentucky No. 13	8.1	95	5	0
Illinois No. 6	10.7	93	5	2
Indiana VI	15.7	96	4	0

## CONCLUSIONS

The distribution of ash compositions in single particles of coal fed to fluidized bed gasifiers governs the amount and particle size of low-melting ash immediately available as agglomerating medium after burnoff of char from the particles. We have investigated the distribution in the 1/4-inch top size coal from several sources by chemical analysis, for ash content and calcium and iron oxides content of the ash, of 32 particles of the -10+12 mesh fractions of the coals. The distributions, though probably not very accurate, show substantial differences among the coals that were investigated. For example, much of the calcium oxide of the coal, as shown by the conventional analysis for major and minor oxides, was missing from a Kentucky No. 9 seam coal and from an Illinois No. 6 seam coal; the loss was attributed to the presence of calcite in the cleat of the coals, resulting in its attrition from the particles in crushing and other handling. Pyrite in the cleat was similarly lost from particles of some of the coals. Other differences in distribution were also evident; the Kentucky No. 9 coal had a substantial amount of ash with ferric oxide content between 20 and 80 weight percent whereas a Pittsburgh No. 8 coal from Ohio had little of this, although its average iron oxide content was much higher.

Etching by oxygen plasma of 1-1/2-inch pieces of the Kentucky No. 9 coal, sectioned normal to the bedding and lightly polished, furnished a striking display of the prevalence of minerals in the attrital layers of coal and its virtual absence in vitrain, except that the presence of thin plates of calcite in the cleat of the vitrain was clearly evident.

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#### REFERENCES CITED

1. Mason, D. M. and Patel, J. G., "Chemistry of Ash Agglomeration in the U-GAS® Process," Fuel Processing Technology **3**, 181-206 (1980).
2. Institute of Gas Technology, "Coal Gasification Research Studies," Washington: U.S. Department of Energy, DOE/MC-19301-10, November 1985.
3. Carty, R. H., Mason, D. M. and Babu, S. P., "Reaction Kinetics and Physical Mechanisms of Ash Agglomeration," Washington: U.S. Department of Energy, DOE/MC/61075. To be published in 1987.
4. Moza, A. K. and Austin, L. G., "Analysis of Pulverized Coal Particles (10-100  $\mu$ m) for Fe, S, Ca, Si and Al on a Particle-by-Particle Basis," Fuel **62**, 1468-73 (1983).
5. Kuhn, J. K., Fiene, F. and Harvey, R., "Geochemical Evaluation and Characterization of a Pittsburgh No. 8 and a Rosebud Seam Coal," Report METC/CR-78/8, 1978.
6. Chadwick, R. A., Rice, R. C., Bennett, C. M. and Woodruff, R. A., "Sulfur and Trace Elements in the Rosebud and McKay Coal Seams, Colstrip Field, Montana," Mont. Geol. Soc. Ann. Field Conf. Guide. **22**, 167-75 (1975).

## APPENDIX

### Method of Analysis of Single Particles

Thirty-two coal particles were randomly selected, and individually ashed overnight (16 to 20 hours) in small Pt-5% Au boats. The boats were specially fabricated for this experiment by cutting a 0.006-inch thick Pt-5% Au crucible into 10 X 10 mm squares and folding up all sides to form boxes in the shape of cubes. A Cahn automatic electrobalance Model 25 was employed to obtain the particle and ash weights. The crucible plus ash was dropped into an acid-cleaned 10 ml volumetric flask to which 5 ml of 6N HCl was then added. The flasks were heated on a hot plate to the boiling point until the reddish color of the oxidized iron from the ashed particle solids had disappeared. Cesium chloride and lanthanum chloride solutions were added to the volumetric flask to obtain a final concentration of 1000 mg/l and 2500 mg/l, respectively, as the metal. The volumetric flask was then diluted to volume using double-distilled water. The volume of the Pt-Au crucible did not contribute any significant volume to the solution. The standards were diluted from commercially obtained stock solutions of iron and calcium, and were made to contain Cs, La and HCl matrices the same as those of the samples. Both iron and calcium were determined by atomic absorption spectrophotometry using a Perkin-Elmer 305B double beam instrument.

An observation was made that the coal particles were not completely destroyed by the ashing and acid treatment. Subsequently, the residual solids of the first coal analyzed were collected and analyzed by X-ray fluorescence spectrophotometry utilizing a Phillips 3100 X-ray generator and a PW1410 X-ray spectrometer. Silica was found to be the major constituent. Iron and calcium were found in trace quantities, however their quantities were negligible in comparison with those determined by HCl leaching.

### LTA Etching

Pieces of coal about 1-1/2-inch in size were cut across the bedding, and the resulting section was lightly polished and cemented to a 1 X 2-inch glass slide. A parallel cut was made to obtain a section 1/8- to 1/4-inch thick; the top surface was polished by thin section techniques to a final polish with 1000 grit diamond impregnated on a metal disc.

After drying in a vacuum oven the section was exposed for periods of 15 minutes to an hour in an oxygen-plasma LTA asher.



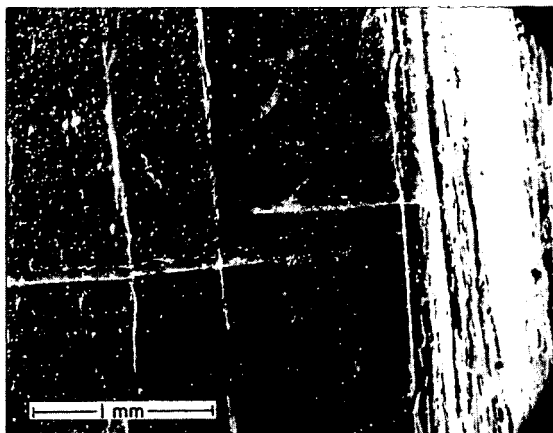


Figure 1. PHOTOMICROGRAPH OF LTA ETCHED KENTUCKY NO. 9 COAL

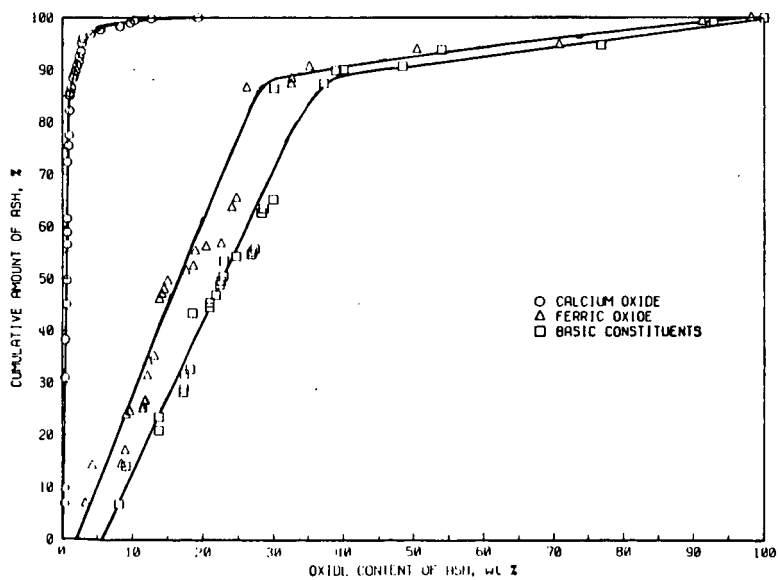


Figure 2. DISTRIBUTION OF BASIC OXIDES IN PARTICLES OF KENTUCKY NO. 9 COAL

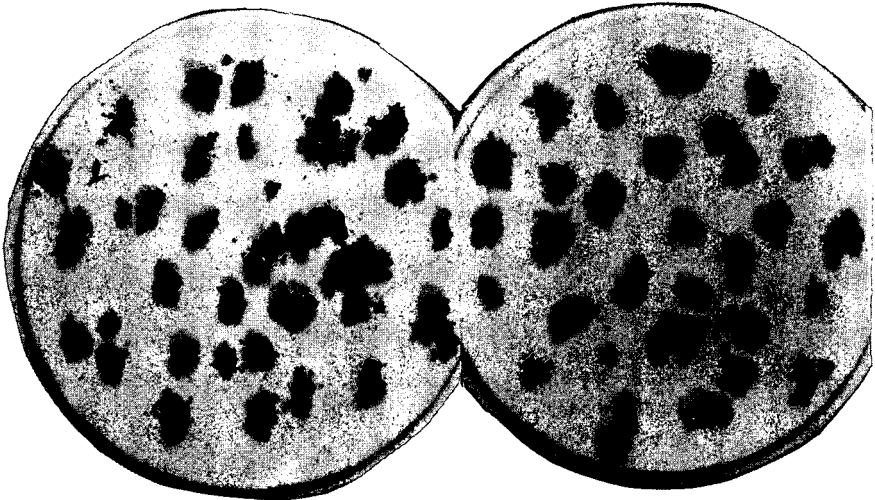


Figure 3. ASH FROM -4+5 MESH PARTICLES OF KENTUCKY NO. 9 COAL

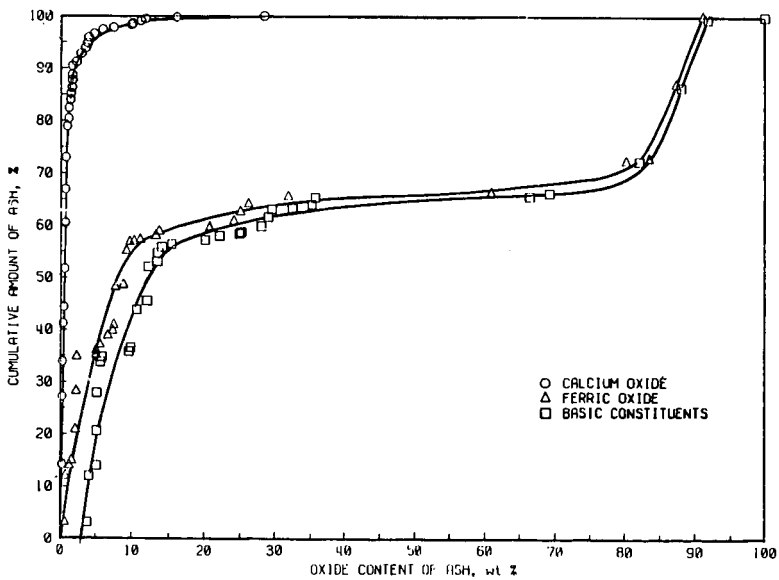


Figure 4. DISTRIBUTION OF BASIC OXIDES IN PARTICLES OF PITTSBURGH NO. 8 COAL

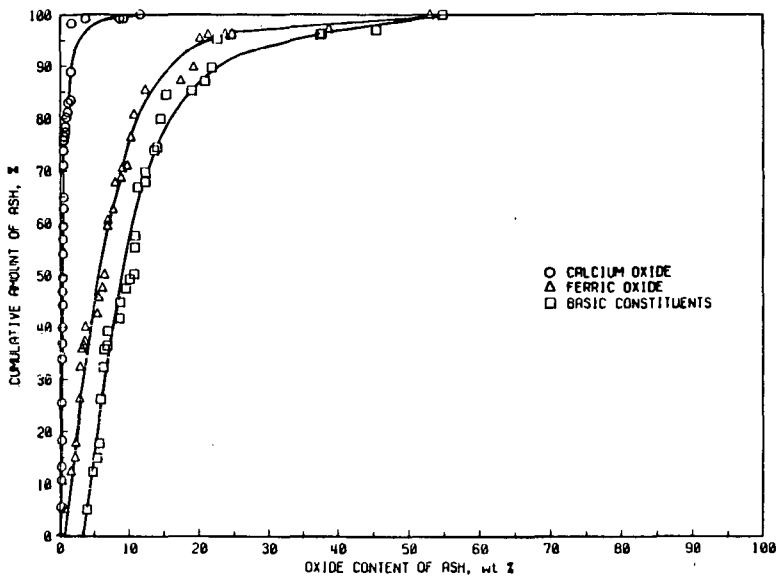


Figure 5. DISTRIBUTION OF BASIC OXIDES IN PARTICLES OF KENTUCKY NO. 13 COAL

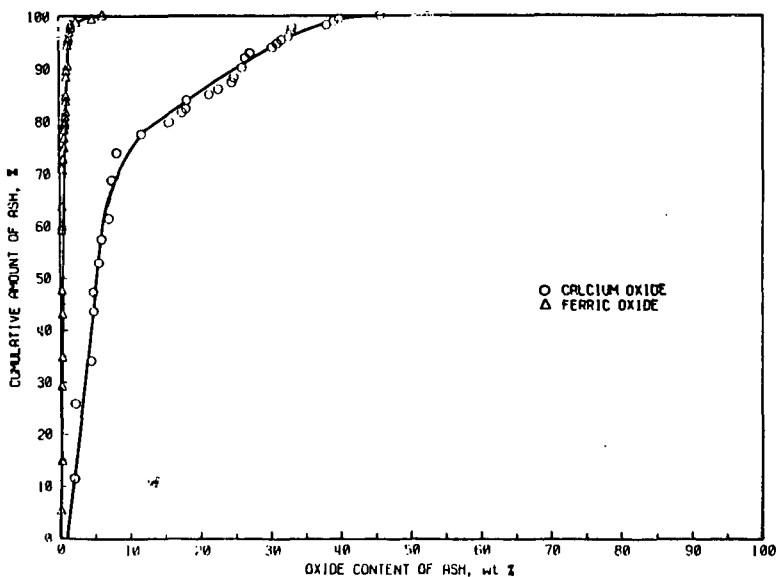


Figure 6. DISTRIBUTION OF FERRIC OXIDE AND CALCIUM OXIDE IN PARTICLES OF ROSEBUD COAL